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PHOTOCHEMICAL REDUCTION OF para-SUBSTITUTED NITROBENZENES IN ISOPROPANOL*

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Hurley and Testa (1) have reported that nitrobenzene in the degassed isopropanol solution is photoreduced from its n-π* excited state to give phenylhydroxylamine, and the quantum yield of the disappearance of nitrobenzene is 1.14×10^{-2}. In analogy with nitrobenzene, α-nitronaphthalene (2), 4-nitropyridine 1-oxide (3), and 4-nitropyridine (4) are reduced photochemically in the hydrogen-donative alcohols to the corresponding hydroxylamino compounds.

In this work, we have found that the kinds of the photoreduction products and the quantum yields of the nitrobenzenes disappearance vary with the substituent effects, when the isopropanol solutions of para-substituted nitrobenzenes are irradiated at the 316 mμ light under nitrogen atmosphere at room temperature.

para-Substituted nitrobenzenes ($p\text{-}XC_6H_4NO_2$) used were as follows:
X; CN, $COOC_2H_5$, $COOCH(CH_3)_2$, COOH, H, CH_3, OCH_3

The identification of the products was performed by measuring the progressive ultraviolet spectral change of para-substituted nitrobenzenes on full-irradiation with a 130 W. immersion type high-pressure mercury lamp under nitrogen atmosphere at room temperature (note: the initial concentration of nitrobenzenes was 1×10^{-3} M in all cases). In most of the reactions, a few isosbestic points were observed. In the experiments of the determination of the quantum yields, the 316 mμ light was isolated from a 130 W. high-pressure mercury lamp with a combination filter of Toshiba UV-D25, aqueous nickel sulfate solution, and carbon tetrachloride. The

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potassium ferrioxalate actinomater was used to determine the quantum yields of the disappearance of nitrobenzenes. The disappearance of nitrobenzenes was determined by measuring optical densities of photolyzed solutions.

The results obtained are summarized in TABLE I.

TABLE I

Reduction Products and Quantum Yields of The Disappearance of *para*-Substituted Nitrobenzenes

p-$XC_6H_4NO_2$ (λ_{max}^{IPA}, $\varepsilon \times 10^{-4}$)	Concn, $\times 10^3$ M	Product (λ_{max}^{IPA})	Quantum Yield
X; CN (256 mμ, 1.33)	1.03	p-Aminobenzonitrile (277 mμ)	0.48
$COOC_2H_5$ (257 mμ, 1.34)	1.00	Ethyl p-aminobenzoate (293 mμ)	0.15
$COOCH(CH_3)_2$ (256 mμ, 1.29)	0.25	Isopropyl p-aminobenzoate (293 mμ)	0.15
COOH (258 mμ, 1.20)	1.00	p-Aminobenzoic acid (288 mμ)	0.12
H (255 mu, 0.756)	1.10	Phenylhydroxylamine (237 mμ)	0.03
CH_3 (270 mμ, 1.05)	1.00	p-Hydroxylaminotoluene (237 mμ)	0.07
OCH_3 (300 mμ, 1.11)	0.25	p-Hydroxylaminoanisole (238 mμ)	0.02

As TABLE I shows, the correspondingly substituted anilines generated from the photoreduction of *para*-substituted nitrobenzenes with electron-withdrawing groups. By the way, *para*-substituted nitrobenzenes with electron-donating groups and nitrobenzene gave the correspondingly substituted phenylhydroxylamines. The other examples of the simple anilines formation in the photolysis of nitroaromatics in ethanol have been reported by Finnegan and Knutson (5) as summarized as follows:

ethyl p-nitrobenzoate ⟶ ethyl p-aminobenzoate (32% yield)
ethyl m-nitrobenzoate ⟶ ethyl m-aminobenzoate (24% yield)
t-butyl p-nitrobenzoate ⟶ t-butyl p-aminobenzoate (52% yield)
p-nitroacetophenone ⟶ p-aminoacetophenone (16% yield)
nitrobenzene ⟶ aniline (13% yield)

Hydrogen-abstruction processes of photoexcited nitrobenzene to form phenylhydroxylamine have been postulated by Hurley and Testa (1). In the anilines formation in the photolysis of substituted nitrobenzenes with electron-withdrawing groups, p-$XC_6H_4N\dot{O}_2H$ radicals may also generate in the primary steps of hydrogen-abstruction.

Meanwhile, the quantum yields of the disappearance of para-substituted nitrobenzenes with electron-withdrawing groups were greater than that of para-substituted nitrobenzenes with electron-donating groups and nitrobenzene. A plot of log-values of the relative quantum yields ($\log\frac{\Phi_X}{\Phi_H}$) of para-substituted nitrobenzenes to nitrobenzene vs. the Hammett constants is shown in Figure 1. The quantum yields

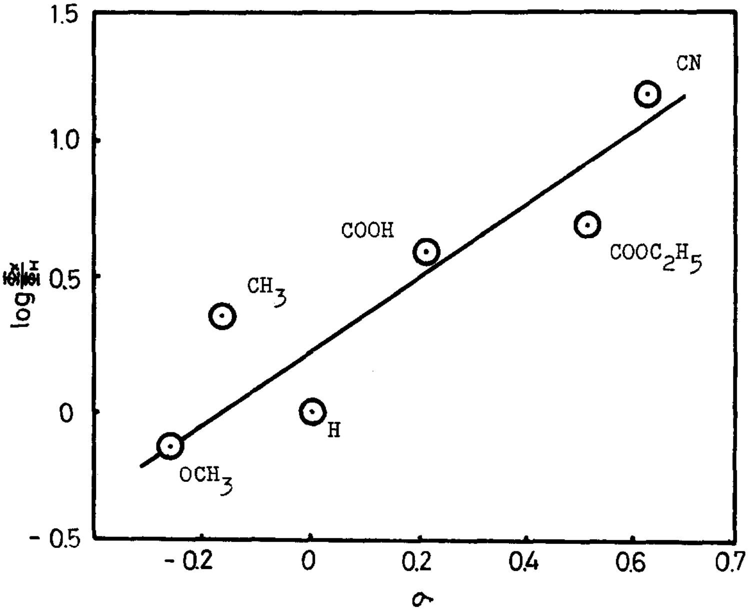

Figure 1. Plot of $\log\frac{\Phi_X}{\Phi_H}$ vs. Hammett Constants

of the disappearance of nitrobenzenes decreased when the photolysis was done in the air-saturated isopropanol. Particularly, the quenching effects by oxygen were remarkable in the photoreduction of nitrobenzenes with electron-withdrawing groups. It suggests that the photoreduction of nitrobenzenes with substituents on parapositions in isopropanol proceeds from the photoexcited triplet states.

From the results obtained, it seems reasonable to assume that hydrogen-abstruction by *para*-substituted nitrobenzenes proceeds electrophilically. The photoreduction of *para*-substituted nitrobenzenes in isopropanol is differ from that of substituted benzophenones in which there is a wide variation in reactivity (6) and is analogous to hydrogen-abstruction reaction of radical $\cdot R\cdot$ which proceeds electrophilically. However, it should take into consideration of lifetime and/or intersystem crossing efficiencies of photoexcited nitrobenzenes to discuss the reactivity of the photoreduction and formula of nitroaromatics in photoexcited states.

Further discussion will be reported later in more detail.

References

1. R. Hurley and A. C. Testa, *J. Am.Chem. Soc.*, **88**, 4330 (1966).
2. S. Hashimoto and K. Kano, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **72**, 188 (1969).
3. C. Kaneko, S. Yamada, I. Yokoe, N. Hata and Y. Ubukata, *Tetrahedron Letters*, 1966, 4729.
4. S. Hashimoto, K. Kano and K. Ueda, *ibid.*, 1969, 2733.
5. R. A. Finnegan and D. Knutson, *J. Am. Chem. Soc.*, **90**, 1670 (1968).
6. N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p.144.